

Life cycle assessment of mineral oil-based and vegetable oil-based hydraulic fluids including comparison of biocatalytic and conventional production methods

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Abstract

Background, aim and scope Lubricants are used in numerous applications in our society, for instance, as hydraulic fluids. When used in forestry, 60–80% of these hydraulic fluids are released into the environment. This is one of the reasons for the growing interest for developing and utilising hydraulic fluids with good environmental performance. Another driving force in the development of hydraulic fluids is to replace fossil products with renewable ones. The aim of this paper is to investigate the environmental impact of two types of hydraulic fluids, one based on mineral oil and one on vegetable oil. The difference in environmental impact of using chemical or biocatalytic production methods is also assessed.

Materials and methods This life cycle assessment is from cradle-to-gate, including waste treatment. A complementary, laboratory, biodegradability test was also performed. The functional unit is 1 l of base fluid for hydraulic fluids, and mass allocation is applied. A sensitivity analysis is performed to assess the impact of the energy used and of the allocation method. The impact categories studied are primary energy consumption, global warming potential (GWP), eutrophication potential (EP), acidification potential (AP), photooxidant creation potential (POCP) and biodegradability.

Results and discussion The contribution to GWP and primary energy consumption was higher for the mineral oil-based hydraulic fluid than the vegetable oil-based hydraulic fluids. The contributions to EP and AP were higher for the vegetable oil-based hydraulic fluid than the

mineral oil-based one. The vegetable oil-based hydraulic fluid had better biodegradability than the one based on mineral oil. The impact of production method was minor, thus the biocatalytic method gives no significant advantage over chemical methods concerning energy and environmental performance.

Conclusions For the environmental impact categories GWP, POCP and primary energy consumption, hydraulic fluids based on rapeseed oil make a lower contribution than a mineral oil-based hydraulic fluid. For EP and AP, the contributions of TMP oleate are higher than the contribution of mineral oil-based hydraulic fluid. The difference between the chemically catalysed method and the enzymatically catalysed method is negligible because the major environmental impact is due to the production of the raw materials. The vegetable oil-based hydraulic fluid, TMP oleate, was more biodegradable than the mineral oil-based hydraulic fluid.

Keywords Biocatalytic production · Biodegradability · Biolubricants · Hydraulic fluids · Life cycle assessment · Rapeseed oil · Trimethylolpropane (TMP)

1 Introduction

Lubricants have been used for millennia to reduce friction and wear. Hydraulic fluids belong to the category of industrial lubricants and are used to transfer power in hydraulic machinery, i.e. excavators, air craft flight control systems and forest machinery. In Sweden, about 30,000 m³ of hydraulic fluids are used annually, of which 50% in forestry (Norrbby and Kopp 2000). About 60–80% of all hydraulic fluids used are released into the environment due to spills and leakages (Schneider 2006; Nilsson 2006). It is

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therefore important, especially in forestry where hydraulic fluids come into close contact with biological systems, to use hydraulic fluids with good environmental properties (Norrby and Kopp 2000; Schneider 2006). To increase the share of environmentally acceptable lubricants, environmental labelling has been introduced both on the national and the international levels (European Commission 2005; Schneider 2006).

Lubricants and hydraulic fluids consist of a base fluid and additives, which are used to improve the technical properties. The amount of additives varies from a few ppm up to 30% of the lubricant, depending on its application. In hydraulic fluids, the amount of additives is generally small (Möller and Young 2007). Base fluids for hydraulic fluids are usually derived from crude oil. An increasing trend is to use synthetic base fluids, either polyalpha olefins or synthetic esters, the latter produced from either fossil or vegetable raw materials (Pettersson 2007). When vegetable oil-based lubricants were first tried, during the oil crises in the 1970s and 1980s, they caused many technical problems. At that time mineral oil-based products were often replaced by pure vegetable oils without the difference in technical properties being considered. Modern vegetable oil-based hydraulic fluids are usually esters of fatty acids from a vegetable oil and branched polyols such as trimethylolpropane (TMP), neopentyl glycol or pentaerythritol. The technical performance of these products is equivalent to the performance of oils derived from petroleum sources (Pettersson 2007; Norrby and Kopp 2000; Willing 2001; Schneider 2006).

In Europe, the most commonly used raw material for vegetable oil-based hydraulic fluids is rapeseed oil. Rapeseed oil is not only locally available; it also has a high content of monounsaturated fatty acids, which provide good technical properties. The price of vegetable oil-based synthetic esters is still high compared to mineral oil-based hydraulic fluids (Schneider 2006; Norrby and Kopp 2000).

Apart from using renewable feedstock, the introduction of biocatalytic processes in their manufacture could prove to be an additional strategy in improving the environmental performance of biolubricants. Previous studies of various green chemical production systems have often shown advantages in the form of improved energy efficiency, reduced feedstock demand, waste minimisation etc. when biocatalytic processes replace conventional chemical processes (Tufvesson and Börjesson 2008; Hatti-Kaul et al. 2007). Although some previous and dedicated life cycle assessments of vegetable oil-based lubricants exist, none has included biocatalytic processes (McManus 2001; Våg et al. 2002).

In this study, (a) a mineral oil-based hydraulic fluid, (b) a vegetable oil-based synthetic ester produced by a chemical process and (c) a vegetable oil-based synthetic ester

produced by an enzymatic process are analysed from a life-cycle perspective. The objective is to compare the products and the production processes regarding various environmental aspects, also including biodegradability, and to identify the most critical parameters from an environmental point-of-view.

2 Methods and assumptions

The study uses life cycle assessment (LCA) following the standards ISO 14040:2006 and ISO 14044:2006. An arbitrary mineral oil-based hydraulic fluid and the rapeseed oil-based hydraulic fluid, TMP oleate, are studied. TMP oleate is one of the vegetable oil-based synthetic esters that are most commonly used as base fluid for hydraulic fluids. Two alternative processes for the production of TMP oleate are compared. The first process is used commercially today, adopting a conventional method based on chemical catalysis. The second process adopts enzymatic catalysis but is still under development. The LCA is from cradle-to-gate but includes biodegradation of the product released into the environment and waste treatment of the recovered, used product.

2.1 Functional unit

The functional unit is 1 l base fluid for hydraulic fluids. Technical performance and life-time per unit volume are assumed to be equal for all products studied. The density of a mineral oil-based hydraulic fluid is 880 kg/m³ (Nordling and Österman 1999) and the density of TMP oleate is 920 kg/m³ (Binol 2010).

2.2 System boundaries

In this study, the production of base fluids for hydraulic fluids is located in Western Europe. Additives are not included in this LCA since focus is on the base fluids. The amount of additives is usually small (Lämsä M, personal communication, January 14, 2009; Möller and Young 2007), and their contributions to the environmental effects studied in this paper are assumed to be negligible. However, additives might have a negative impact on the ecotoxicity of hydraulic fluids but this is not within the scope of this analysis. The cultivation of rapeseed as well as the production of rapeseed oil takes place in Denmark. LCI data for rapeseed cultivation are taken from Schmidt (2007) and include field emissions of N₂O calculated according to IPCC (2006) based on average values for distribution on sandy and clay soil in Denmark. The average application of N fertiliser is 140 kg N/ha and the production of fertiliser causes emissions of 9.05 kg CO₂eq/kg N

fertiliser as N mainly in the form of emissions of N_2O . The nutrient leakage is 52 g NO_3/kg rapeseed. Biogenic CO_2 emissions are not included. Cultivation of rapeseed is not connected with land-use changes, and therefore, potential CO_2 emissions caused by land transformations are not included (Schmidt 2007). Natural gas (Uppenberg et al. 2001) is used for heating and steam generation in the production of vegetable oil-based base fluids. The European electricity mix is used in all processes (Mårtensson and Svensson 2009).

The extraction of crude oil takes place in the Middle East. In the refining of oil and the production of mineral oil-based lubricants, refinery by-products are used as the energy supply. In a sensitivity analysis, the impact of transports as well as of using less carbon intensive energy sources is studied. The primary energy factors and impact on global warming from the different energy sources are presented in Table 1. The rate of recovery of waste hydraulic fluids is assumed to be 30%, based on current practical conditions (Schneider 2006). Although the biodegradation of mineral oil is probably slower than that of vegetable oils, the oil will eventually be degraded to CO_2 and water. Since hydraulic fluids cannot be degraded under anaerobic conditions, emissions of methane from the degradation of oil are not considered (Willing 2001). Based on Swedish conditions, the waste hydraulic fluids recovered are assumed to be incinerated under specified conditions (SFS 1993:1268). The distribution and use of hydraulic fluids are not included because these processes are assumed to be equal for all products. The construction and maintenance of the refinery and other facilities are not considered in this study.

2.3 Allocations

Mass allocation has been used throughout the study. In the sensitivity analysis, the impact of using economic allocation in the production of vegetable oil-based hydraulic fluids is studied.

2.4 Impact categories

The environmental impact categories studied are primary energy consumption, global warming potential (GWP), acidification potential (AP), eutrophication potential (EP),

photooxidant creation potential (POCP) and biodegradability. The characterisation factors are those recommended by IPCC (2006) and Solomon et al. (2007).

2.5 Measurement of biodegradability

Biodegradability implies that a substance can be degraded by living organisms, and ready biodegradability means complete mineralisation to CO_2 and water. For this study, ready biodegradability is tested by the test method OECD 301 B, which is the preferred test for ready biodegradability of poorly water-soluble fluids. The test procedure is described in the *OECD Guideline for Testing of Chemicals* (1992). For this, the test substance was mixed with mineral medium and activated sludge, and the mineralisation of the test substance was measured as production of CO_2 . Ultrasonication was used to disperse the oil in the mineral medium. The CO_2 concentrations in the gas phase were measured by gas chromatography. The substances tested were a mineral oil-based hydraulic fluid Texaco Rando HDZ 32, TMP oleate provided by Binol AB (AAK) and an enzymatically produced TMP oleate produced at the Department of Biotechnology at Lund University.

3 System descriptions

3.1 Mineral oil-based hydraulic fluid

Base stock for mineral oil-based lubricants is produced from the high boiling-point fraction of crude oil (Wang et al. 2004). The mineral oil-based base fluid for hydraulic fluid is assumed to have been produced from a paraffinic base stock using solvent extraction, which is still the most common method for the production of lubricants (Lynch 2008). The production system studied for mineral oil-based hydraulic fluids is illustrated in Fig. 1. LCI data for the extraction of crude oil are taken from Boustead (2005e). Oil refining in this study includes two steps, atmospheric distillation and vacuum distillation. Lubricant production includes the processes, solvent de-asphalting, solvent extraction, solvent dewaxing, solvent recovery and hydro-treatment (Lynch 2008; Bartels et al. 2005; Energetics Incorporated 2007). The energy consumption in the refining and lubricant production processes is calculated according

Table 1 Primary energy consumption and greenhouse-gas emissions for energy sources

Energy source	Primary Energy (MJ/MJ)	GWP (g CO_2 eq/MJ)
EU average electricity	2.2 ^a	110 ^a
Swedish average electricity	2.0 ^b	11 ^b
Natural gas-based heat	1.15 ^c	63 ^c
Wood chip-based heat	1.20 ^c	3.7 ^c

^a Mårtensson and Svensson 2009

^b Lantz et al. 2009

^c Uppenberg et al. 2001

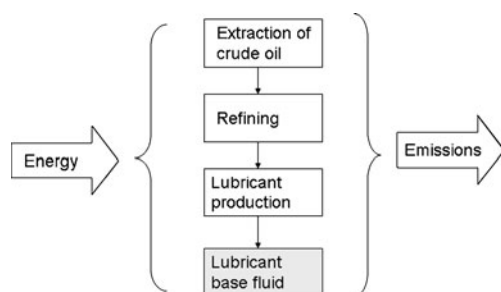


Fig. 1 Schematic diagram of the production of mineral oil-based hydraulic fluid

to Energetics Incorporated (2007), and the emissions are calculated by the emission factors given by the Swedish Environmental Protection Agency (2009). The production of the solvents used in these processes is also included in the lubricant production. In this study, the solvents used in the lubricant production (propylene, phenol, toluene and pentane) are assumed to be produced in Europe and the LCI data for solvents are taken from Boustead (2005a, b, c, d). In the calculations, solvents are recycled 20 times, an assumption based on Energetics Incorporated (2007).

3.2 Vegetable oil-based hydraulic fluid

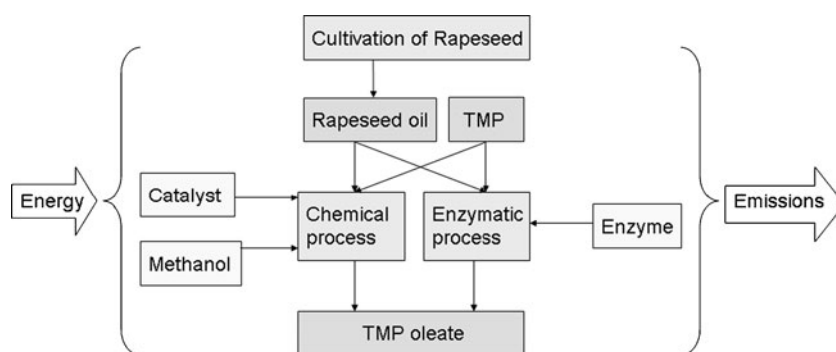
The production of TMP oleate is shown schematically in Fig. 2. Rapeseed is cultivated in Denmark, where the average yield is 3,131 kg seed per hectare and the cultivation is not expected to induce land-use changes (Schmidt 2007). Pressing and hexane extraction produce 45% oil and 55% rapeseed meal (Cederberg and Flysjö 2008; Bernesson et al. 2004). Straw is not included in this study. TMP is a six carbon, branched polyol with three hydroxyl groups. The raw materials for TMP are mainly derived from natural gas. TMP is produced by Perstorp AB, Sweden. The production of TMP is assumed to be similar to the production of other polyols (Andersson and Severinsson 1996).

Chemically catalysed production of TMP oleate is a two-step reaction described by Lämsä (1996). In the first step, rapeseed oil is made to react with methanol to form

rapeseed methyl ester (RME). Methanol is produced from natural gas, and the RME is produced by conventional methods for biodiesel production (Bernesson et al. 2004; Mårtensson and Svensson 2009). In the second step, RME reacts with TMP to form TMP oleate. The molar ratio of the reactants in the second transesterification step is 1:3.5 (TMP/RME). The reaction temperature is between 100°C and 140°C, and the total reaction time is 17 h (Lämsä 1996). Unreacted RME and methanol are recycled with 5% losses in each cycle. The maximum yield of the process is 99% (Uosukainen et al. 1998). Heating requirements for the processes are calculated by established thermodynamic equations (Welty et al. 2001). The reactions are carried out in continuously stirred, insulated batch reactors of stainless steel. The reaction volume is 1,000 l and the ratio of radius-to-height is 1:3.

The biocatalytic process has been developed at Lund University and is described by Orellana Coca et al. (2011). The first step is the hydrolysis of rapeseed oil, a process with an energy requirement of 140 kWh, 50% electricity and 50% steam per ton rapeseed oil (Tufvesson and Börjesson 2008). Data for biocatalytic esterification are based on a laboratory scale reaction, scaled up theoretically. The reaction temperature is 70°C. In the base case, the reaction time is 24 h. The process yield is 97%, and the remaining fatty acid and TMP are part of the final product. Vacuum is applied to remove the water formed (Orellana Coca et al. 2011). The enzyme concentration is 5% by weight, and the LCI data for the enzyme are taken from Nielsen et al. (2007). After the reaction, the enzyme is removed by filtration. The enzyme is assumed to be recycled 25 times. The electricity consumption is calculated according to a biochemical sample process of similar scale (Blanch and Clark 1997). The enzymatically catalysed reaction is assumed to be carried out in the same type of reactors as the chemically catalysed production, and the heat requirement is calculated using the same equation. Both one- and two-step reactions are being used commercially. Using a chemical catalyst, the two-step method can give a higher yield of TMP triesters than the one-step

Fig. 2 Schematic diagram of the production of TMP oleate



reaction even under relatively mild reaction conditions (Lämsä 1996). This makes the two-step reaction more suitable for comparison with the new enzymatic method.

4 Results

4.1 Primary energy consumption

The consumption of primary energy for the production of mineral oil-based hydraulic fluids is more than twice for the rapeseed oil-based TMP oleate (Fig. 3). Lubricant production, including solvents, is a very energy-intensive process. For the vegetable oil-based hydraulic fluids, the production of rapeseed oil and TMP account for the major part of the energy consumption. The energy balance is significantly affected by the amount of energy that can be recovered after the hydraulic fluids have been used.

The contribution to global warming is approximately four times higher for the mineral oil-based hydraulic fluid than for TMP oleate (Fig. 4). For TMP oleate, field emissions of nitrous oxide in rapeseed cultivation give an important contribution to global warming. Greenhouse gases released in waste treatment are due to fossil carbon in the TMP and in mineral oil-based hydraulic fluids.

The contributions to acidification (Fig. 5) are approximately 50% higher for vegetable oil-based hydraulic fluids than for mineral oil-based hydraulic fluids due to high emissions from rapeseed cultivation. Concerning the mineral oil-based hydraulic fluid, lubricant production, including solvents, is responsible for the highest impact.

The contributions to eutrophication are significantly higher for vegetable oil-based hydraulic fluids than for

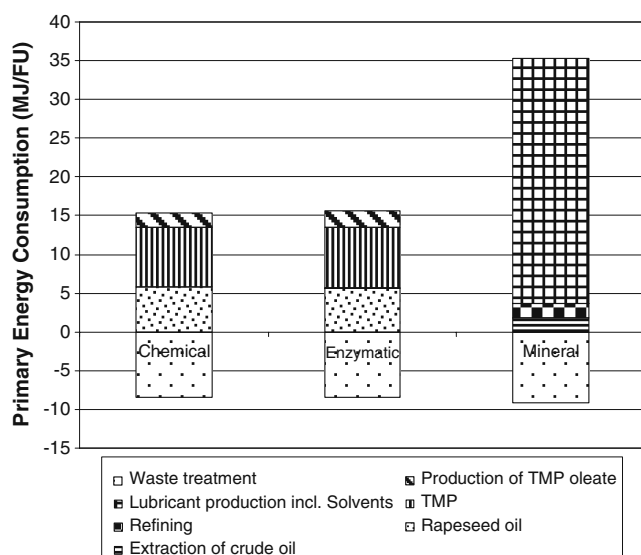


Fig. 3 Primary energy consumption for the production of hydraulic fluids

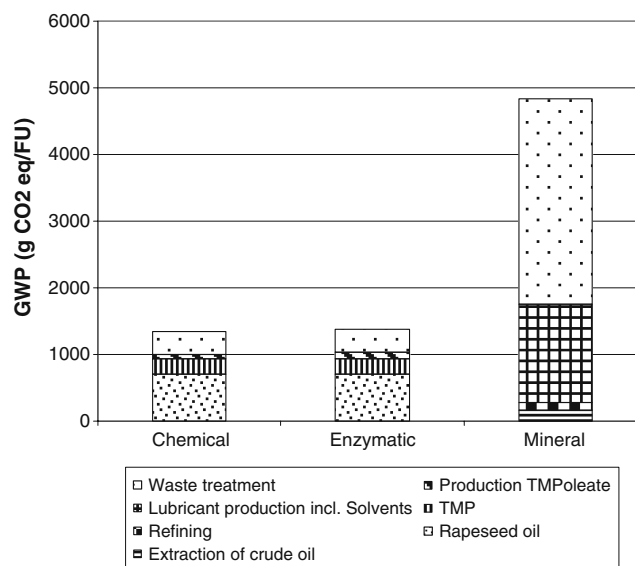


Fig. 4 Contribution to global warming

mineral oil-based ones (Fig. 6). This is mainly due to nutrient leaching in rapeseed cultivation.

The photooxidant creation potential of mineral oil-based hydraulic fluid is roughly eight times higher than that of vegetable oil-based hydraulic fluids (Fig. 7). This originates mainly from the processes in the extraction of crude oil and in lubricant production.

TMP oleate showed better biodegradability than the mineral oil-based hydraulic fluid (Fig. 8). As expected, no significant difference could be seen between the chemically and enzymatically produced TMP oleate.

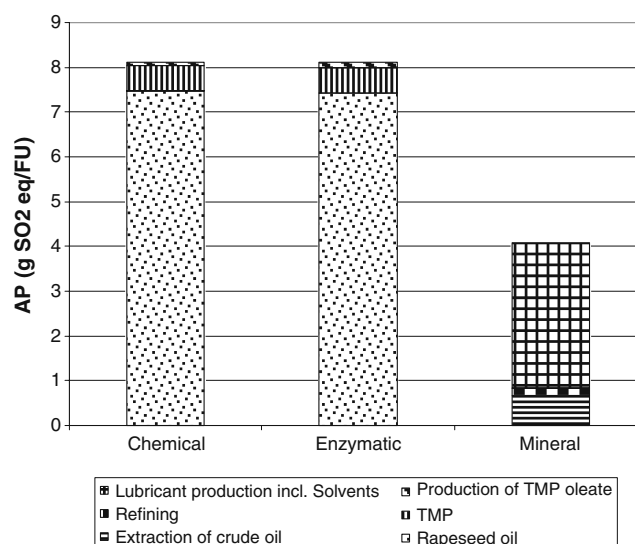


Fig. 5 Contribution to acidification

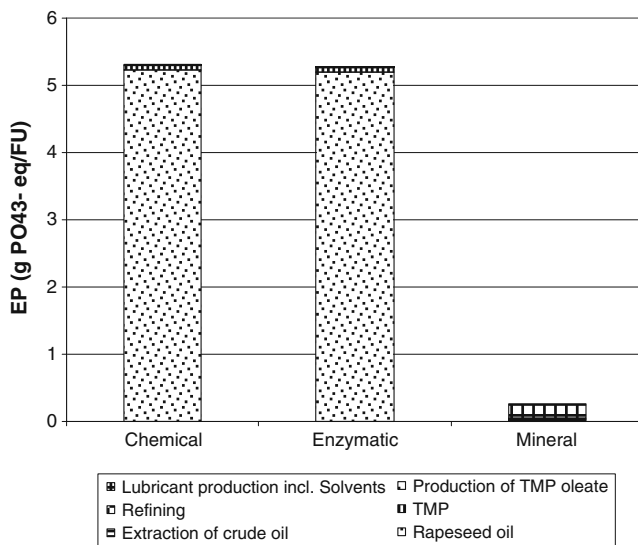


Fig. 6 Contribution to eutrophication

5 Sensitivity analysis

Introducing low-carbon energy which in this study is represented by Swedish average electricity, mainly hydro and nuclear power as well as wood chips for heating purposes, has a relatively limited impact on GWP for vegetable oil-based hydraulic fluids (Fig. 9). Total emissions of greenhouse gases decrease by 3% for both the biocatalytic and the chemically catalysed processes. For mineral oil-based hydraulic fluids, the impact is somewhat higher. For TMP oleate, the major contribution to global warming comes from the cultivation of rapeseed, which is not affected when low-carbon energy is used. Economic allocation increases the contribution to global warming caused by TMP oleate by approximately 30% compared to

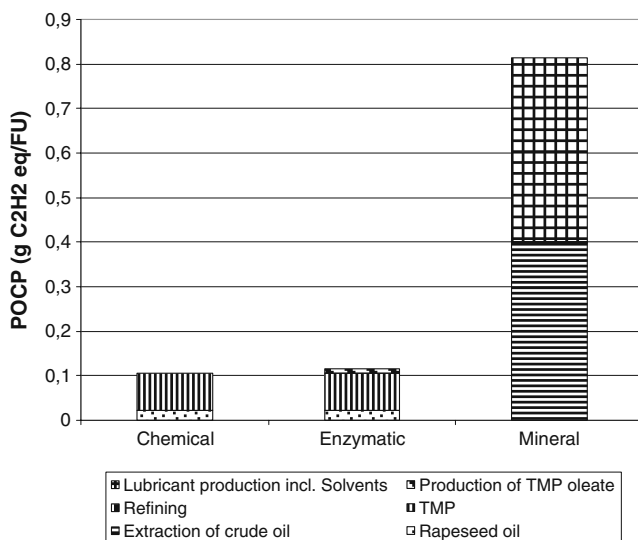


Fig. 7 Contribution to photooxidant creation

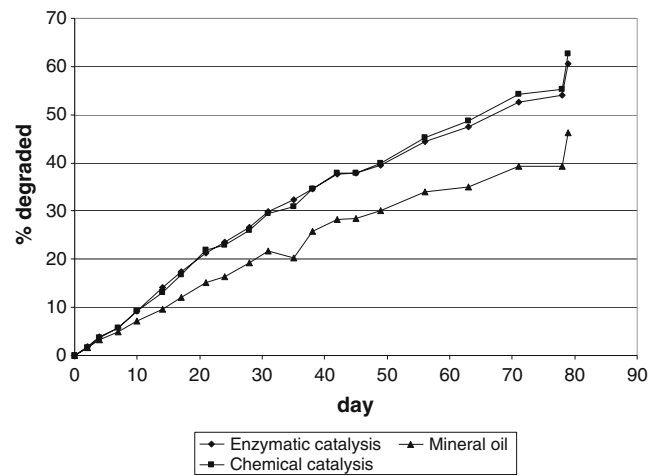


Fig. 8 Biodegradability of hydraulic fluids

mass allocation. In this paper, rapeseed oil gives 72% and rapeseed meal 28% of the contribution to the total economic value of the agricultural products. For the final products, the price of TMP oleate is 98% and the price for glycerol is 2% (Cederberg and Flysjö 2008). These figures are based on the current market situation, but price relations are variable over time, which will affect the environmental performance of the products. Mass allocation, on the other hand, is constant over time, but can be misleading if large amounts of low value by-products are produced in the system. One such possible by-product is straw, which is excluded in this study. Emissions caused by transport, 2,000 km by heavy truck, give a very small additional contribution to GWP.

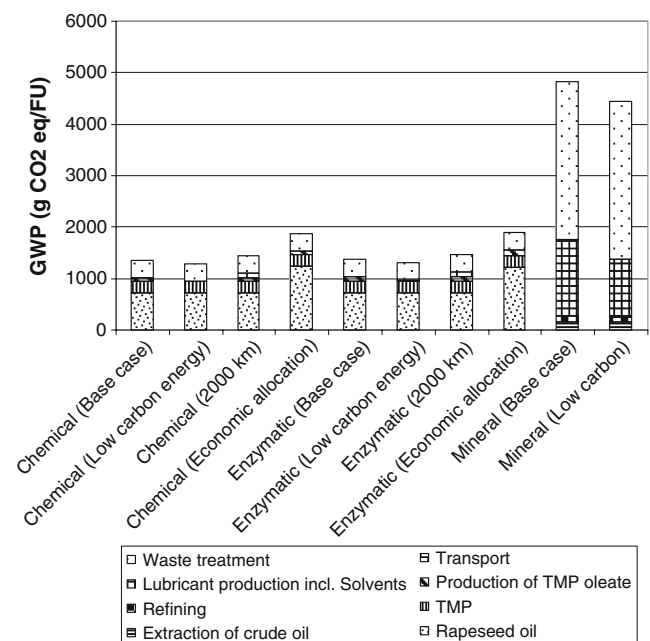


Fig. 9 Sensitivity analysis, contributions to global warming from production of hydraulic fluids

In the cultivation of rapeseed and in the production of rapeseed oil, emissions of nitrous oxide are responsible for more than 50% of the contribution to global warming. There are large uncertainties in the data for these emissions because they depend on the production method of fertilisers, the amount of fertiliser used and variations in local soil conditions. The variations of field emissions of N_2O may be as large as $\pm 50\%$ (Tufvesson and Börjesson 2008). This will affect the total contribution to global warming from vegetable oil-based hydraulic fluids by $\pm 17\%$ for both chemically and enzymatically produced TMP oleate.

Nutrient leaching from arable land is also associated with large uncertainties. Variations may be as large as $\pm 30\%$ depending on soil type, cropping systems and amount and type of fertiliser used (Johnsson and Mårtensson 2002). The variations in nitrogen leaching will affect the eutrophication potential by $\pm 28\%$ for vegetable oil-based hydraulic fluids. For acidification, the effect is $\pm 17\%$ of the total contribution.

6 Discussion

In the evaluation of the environmental impact in green chemistry, it is important to be aware of the diversity of environmental issues connected with a certain product. In recent years, the search for products with a low impact on global warming has been the main focus. This is, of course, a serious issue but it is important not to allow this to override other environmental aspects. For hydraulic fluids, of which huge amounts are lost in the environment, biodegradability is an important environmental aspect which must also be assessed. The biodegradability test in this study confirmed that vegetable oil-based hydraulic fluids have a higher biodegradability than those based on mineral oil. Ecotoxicity is also an important environmental aspect but is probably connected with the additives to lubricants, which are not included in this study. Future analyses in which additives and ecotoxicity are included will therefore be needed.

LCA is an efficient tool with which to find hot spots in the life cycle of a product. As is clearly shown in this study, the dominating environmental impact comes from the raw materials either in the material as such (mineral oil) or from the production of the raw material (rapeseed oil). LCA can therefore be a good help in choosing appropriate raw materials and in improving the production of raw materials. There is an ongoing discussion about the importance and relevance of including potential land-use changes and effects of GWP in LCAs. Regarding a future, large-scale expansion of biofuels and bio-based bulk chemicals, it is important that these issues are considered; see Börjesson and Tufvesson (2010) for a detailed discussion. For

specialty chemicals produced in smaller volumes, such as renewable hydraulic fluids, the amount of land needed for feedstock production is significantly smaller, leading to a minor increase in potential land-use conflicts. In this study, rapeseed is assumed to be cultivated on existing farm land, since this is not fully utilised in Europe. In other cases, for example when permanent grass land is converted into farm land, it is relevant to include direct land-use changes because the GWP for rapeseed oil may then be twice that for rapeseed grown on existing farm land (Börjesson and Tufvesson 2010).

Biocatalytic production could be assumed to be superior to chemical production concerning environmental impact. The advantages of biocatalytic production are the milder reaction conditions such as lower temperatures and pressure and avoidance of organic solvents. This could save energy and increase the yield of the desired products. Biocatalytic processes can also be used for the production of substances that are difficult or impossible to produce by conventional methods or for products with specific properties. In the case of TMP oleate however, there are no important environmental incentives for choosing the one or the other production method. Although there are some uncertainties in the data for the production of TMP oleate, the data used are however, sufficiently good to state that in this case the production step of biolubricants makes a very small contribution to the total environmental impact. The potential energy savings are limited because the lower reaction temperature of the biocatalytic process is outweighed by an increase in electricity consumption due to the longer reaction time. The yield of chemical production is as high as the yield of biocatalytic production and none of the processes include the use of organic solvents or creates toxic by-products. Differences in quality between the chemically and biocatalytically produced TMP oleate are negligible in this case. A typical benefit of enzymatic processes is the specificity of the enzyme, which can help to increase the yield and reduce the formation of by-products. This is especially desirable when toxic compounds or compounds with a negative impact on the quality can be avoided. In this case, however, it will be economic factors on which the choice of the process is based. From an overall environmental point-of-view, the most important factor is that vegetable oil-based hydraulic fluids, irrespective of production method, will become competitive and thereby replace mineral oil-based hydraulic fluids.

7 Conclusions

For the environmental impact categories GWP, POCP and primary energy consumption, hydraulic fluids based on

rapeseed oil make a lower contribution than a mineral oil-based hydraulic fluid. For EP and AP, the contributions of TMP oleate are higher than the contribution of mineral oil-based hydraulic fluid. The difference between the chemically catalysed method and the enzymatically catalysed method is negligible because the major environmental impact is due to the production of the raw materials. The vegetable oil-based hydraulic fluid, TMP oleate, was more biodegradable than the mineral oil-based hydraulic fluid.

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